123. *The Formation of Phenanthroxazole by the Action of Diazomethane on Phenanthraquinoneimine.*

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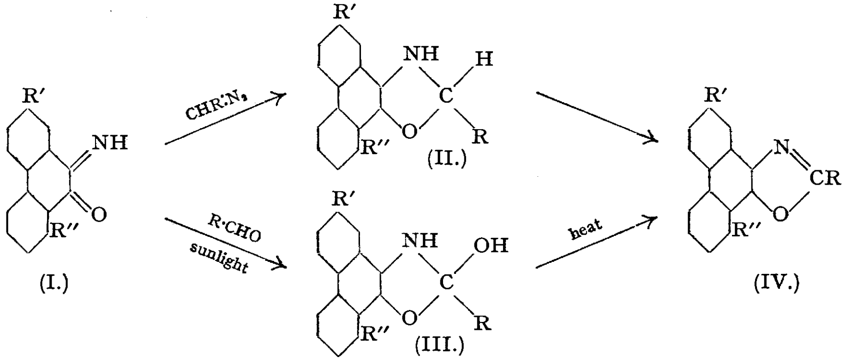
Phenanthraquinoneimine (I; $R' = R'' = H$) when treated with diazomethane yields phenanthroxazole (IV; $R = R' = R'' = H$). The action of diazoethane yields 2-methylphenanthroxazole (IV; $R = Me$, $R' = R'' = H$). Retenequinoneimine (I; $R' = Me$ or Pr^{β}, $R'' = Pr^{\beta}$ or Me) behaves similarly.

Retenequinoneimine in sunlight with acetaldehyde, benzaldehyde, or anisaldehyde yields the substances (III; $R = Me$, Ph, or $C_6H_4{\cdot}OMe$; R' and R'' as above); the first, on being heated, yields 2-methylreteneoxazole (IV; $R = Me$; R' and R'' as above), identical with the product obtained by the action of diazoethane on retenequinoneimine. Similarly, 2-hydroxy-2-methyl-2 : 3-dihydrophenanthroaxazole (III; $R = Me$, $R' = R'' = H$) gives 2-methylphenanthroxazole (IV; $R = Me$, $R' = R'' = H$) on heating, identical with the product obtained from diazoethane and phenanthraquinoneimine.

The product obtained by De and Ghosh by the action of formic acid on 9-amino-10-phenanthrol hydrochloride and described as phenanthroxazole proved to be phenanthroxazine (V).

As far as we are aware, the formation of oxazoles by the method mentioned above or by similar reactions has not hitherto been observed.

When phenanthraquinoneimine (I; $R' = R'' = H$) was treated with diazomethane, phenanthroxazole (IV ; $R = R' = R'' = H$) was obtained and identified by comparison with an authentic sample (Pschorr, *Ber.*, 1902, **35**, 2740). It is believed that the first step in this reaction is the formation of 2 : 3-dihydrophenanthroxazole (II; $R = R' = R'' = H$) which, in consequence of oxidation, yields the oxazole : atmospheric oxygen or phenanthraquinoneimine itself, which is readily reduced to 9-amino-10-phenanthrol (McCoy and Day, *J. Amer. Chem. Soc.*, 1943, **65**, 1956), may serve as oxidising agent.

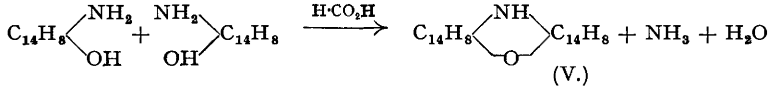


The action of diazoethane on phenanthraquinoneimine yielded *2-methylphenanthroxazole* (IV; R = Me, R′ = R″ = H), the constitution of which was proved by a second synthesis. Phenanthraquinoneimine and acetaldehyde in sunlight yielded 2-hydroxy-2-methyl-2 : 3-dihydrophenanthroxazole (III; R = Me, R′ = R″ = H) (cf. Schönberg and Awad, *J.*, **1945**, 197), which on heating lost water with the formation of the oxazole (as IV), proved to be identical with the product obtained by the action of diazoethane on phenanthraquinoneimine.

The action of diazomethane on retenequinoneimine * yielded reteneoxazole (IV; R = H, R′ = Me and R″ = Pr^{β} or conversely), and diazoethane similarly gave 2-methylreteneoxazole (IV; R = Me, R′ = Me, R″ = Pr^{β}, etc.), the latter also being obtained by the action of acetaldehyde, followed by heat, on the imine.

We have also prepared by the same method from benzaldehyde and anisaldehyde *2-hydroxy-2-phenyl-2 : 3-dihydroreteneoxazole* and its *2-anisyl* analogue, respectively, of type (III).

De and Ghosh stated (*J. Ind. Chem. Soc.*, 1930, **7**, 357) that they obtained phenanthroxazole by interaction of 9-amino-10-phenanthrol hydrochloride and formic acid; they described it as a brown substance, m. p. >300°, but did not give analyses for carbon and hydrogen. Such a high m. p. and deep colour are highly improbable for phenanthroxazole. Moreover, those authors did not mention that Pschorr (*loc. cit.*) had already prepared this oxazole. We believe the substance to be phenanthroxazine (V), produced according to the scheme :



$$C_{14}H_8\Big\langle{}^{NH_2}_{OH} + {}^{NH_2}_{OH}\Big\rangle C_{14}H_8 \xrightarrow{H\cdot CO_2H} C_{14}H_8\Big\langle{}^{NH}_{O}\Big\rangle C_{14}H_8 + NH_3 + H_2O$$

(V.)

De and Ghosh also stated that they obtained 2-methylphenanthroxazole by the use of acetic acid instead of formic acid. As the substance is brown with m. p. >300°, such a constitution is improbable. The true 2-methylphenanthroxazole is described above.

EXPERIMENTAL.

Action of Diazomethane.—(a) *On phenanthraquinoneimine.* The imine, suspended in dry ether, was treated in the cold with an ethereal solution of excess of diazomethane (prepared from nitrosomethylurea and aqueous potassium hydroxide). The product was crystallised from methyl alcohol (charcoal) and phenanthroxazole was obtained in light yellow crystals, m. p. 152°, subliming unchanged in a vacuum [Found : C, 82·0; H, 4·2; N, 6·4; *M* (Rast's method), 216. Calc. for $C_{15}H_9ON$: C, 82·2; H, 4·1; N, 6·4%; *M*, 219]. A mixed m. p. with phenanthroxazole prepared according to Pschorr (*loc. cit.*) gave no depression. (Pschorr reported a brownish-yellow product of m. p. 146.°) In the preparation, we followed Pschorr's method, but found it advisable to use 10% sodium hydroxide solution in the methylation of phenanthraquinone monoxime.

(b) *On retenequinoneimine.* The reaction was carried out as above. Reteneoxazole crystallised from methyl alcohol in yellow crystals, m. p. 108° (Jaffe and Day, *J. Org. Chem.*, 1943, **8**, 43, gave m. p. 108°) (Found : C, 82·7; H, 6·1; N, 5·3. Calc. for $C_{19}H_{17}ON$: C, 82·9; H, 6·2; N, 5·1%).

Action of Diazoethane (Werner, *J.*, 1919, **115**, 1093).—(a) *On phenanthraquinoneimine.* The reaction was carried out as with diazomethane and the product was crystallised from methyl alcohol; *2-methylphenanthroxazole* forms light yellow crystals, m. p. 145°. It gives no colour reaction with concentrated sulphuric acid and is insoluble in dilute sodium hydroxide or dilute hydrochloric acid, in both cases

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* The constitution of this imine is uncertain; hence the alternatives for R′ and R″ to correspond with uncertainty in the relative positions of :NH and :O.

in the cold as well as on boiling. It is soluble in boiling benzene (Found : C, 82·2; H, 5·1; N, 6·5. $C_{16}H_{11}ON$ requires C, 82·4; H, 4·7; N, 6·0%).

(b) *On retenequinoneimine.* 2-Methylretenoxazole (IV; R = Me, R′ or R″ = Me or Pr^{β}) was obtained from methyl alcohol in almost colourless crystals, m. p. 135° : Jaffe and Day (*loc. cit.*) gave m. p. 127·5—128·5°. The substance dissolves in concentrated sulphuric acid with a light yellow colour (Found : C, 82·8; H, 6·45; N, 5·0. Calc. for $C_{20}H_{19}ON$: C, 83·0; H, 6·6; N, 4·8%).

Action of Alcoholic Hydrochloric Acid.—(a) *On phenanthroxazole.* 0·1 G. of phenanthroxazole was refluxed with a mixture of 20 c.c. of alcohol and 10 c.c. of hydrochloric acid for 3 hours; on cooling and concentration, orange crystals of phenanthraquinone appeared. It is probable that the above reaction first yields 9-amino-10-phenanthrol, and that this is then changed into 9 : 10-dihydroxyphenanthrene, which is oxidised by the air to phenanthraquinone. We have satisfied ourselves that 9-amino-10-phenanthrol, when treated with alcoholic hydrochloric acid under the conditions mentioned above, yields phenanthraquinone. Furthermore, the aminophenanthrol has been obtained by Pschorr (*loc. cit.*) by the action of hydrochloric acid on phenanthroxazole.

(b) *On reteneoxazole.* The reaction was carried out as above, and retenequinone obtained.

Action of Aldehydes on Retenequinoneimine in Sunlight.—General remarks. The photochemical reactions were carried out in Monax-glass tubes, the air being displaced by dry carbon dioxide, and the tubes sealed by fusion. The benzene was thiophen-free and dried over sodium.

(a) *With benzaldehyde.* Retenequinoneimine (0·5 g.) and benzaldehyde (1 g.) in 50 c.c. of benzene were exposed to sunlight for 2 days (January), the benzene was driven off in a vacuum, and the product repeatedly crystallised from alcohol, in which it is difficultly soluble in the cold; 2-*hydroxy*-2-*phenyl*-2 : 3-*dihydroreteneoxazole* (III; R = Ph, R′, R″ = Me, Pr^{β}) forms almost colourless crystals, m. p. about 168°, with decomposition and a red brown melt (Found : N, 3·8. $C_{25}H_{23}O_2N$ requires N, 3·8%).

(b) *With anisaldehyde.* Retenequinoneimine (0·5 g.) and anisaldehyde (1 g.) in 50 c.c. of benzene were left for one month (February—March). 2-*Hydroxy*-2-*anisyl*-2 : 3-*dihydroreteneoxazole* separated out during the experiment in the form of crystals. It recrystallised from benzene as pale yellow crystals, m. p. 222°, with evolution of gas (Found : C, 77·9; H, 6·1; N, 3·7. $C_{26}H_{25}O_3N$ requires C, 78·2; H, 6·3; N, 3·5%).

(c) *With acetaldehyde.* 0·5 G. of retenequinoneimine and 10 g. of acetaldehyde in 50 c.c. of benzene were exposed for 5 days (April) to sunlight. The product was crystallised from benzene–alcohol, giving almost colourless crystals, m. p. 130°. This substance was pyrolysed for 30 minutes in a stream of dry carbon dioxide, the vessel being immersed in a bath of ethyl cinnamate (b. p. 271°) and fitted with a long side tube externally cooled. The product, which formed crystals on the cold part of the reaction vessel, was crystallised from methyl alcohol; its m. p. of 135° was not depressed on admixture with 2-methyl-reteneoxazole obtained by the action of diazoethane on retenequinoneimine (Found : N, 5·0. Calc. for $C_{20}H_{19}ON$: N, 4·8%).

Pyrolysis of 2-*Hydroxy*-2-*methyl*-2 : 3-*dihydrophenanthroxazole.*—This was carried out as described above. 2-Methylphenanthroxazole was obtained; it crystallised from methyl alcohol and had m. p. and mixed m. p. with the product obtained by the action of diazoethane on phenanthraquinoneimine 145° (Found : C, 81·8; H, 4·7; N, 5·6. Calc. for $C_{16}H_{11}ON$: C, 82·4; H, 4·7; N, 6·0%).

Action of Chromium Trioxide on 2-*Hydroxy*-2-*anisyl*-2 : 3-*dihydroreteneoxazole.*—To the reteneoxazole derivative (0·4 g.) in 50 c.c. of glacial acetic acid, a solution of 0·4 g. of chromium trioxide in 10 c.c. of glacial acetic acid was added, and the mixture heated for 2 hours and then cooled. Water was added, and the precipitate proved to be retenequinone after crystallisation from alcohol–chloroform.

Action of Formic Acid on 9-*Amino*-10-*phenanthrol Hydrochloride.*—The experiment was carried out as described by De and Ghosh (*loc. cit.*). The brown product which separated during heating was isolated and purified by repeated extraction with alcohol; m. p. above 350°. It showed a violet colour with concentrated sulphuric acid (Found : N, 4·0. Calc. for $C_{28}H_{17}ON$: N, 3·7%). Phenanthroxazine was also purified by vacuum sublimation, giving green crystals which became brown after pulverisation (cf. Bamberger and Grob, *Ber.*, 1901, **34**, 533) (Found : N, 3·2. Calc. for $C_{28}H_{17}ON$; N, 3·7%)

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